REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE:	3. REPORT TYPE AND DATES COVERED Final Report 10-Jul-2002 - 9-Jul-2006

4. TITLE AND SUBTITLE

New Tools for Measurement of Personal Exposure to Chemical Environments

5. FUNDING NUMBERS

DAAD190210299

6. AUTHORS

Nicholas L. Abbott

8. PERFORMING ORGANIZATION REPORT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES

University of Wisconsin - Madison
Research and Sponsored Programs
750 University Ave., 4th Fl.
Madison, WI 53706 -1490

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

43602-CH.1

11. SUPPLEMENTARY NOTES

The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12. DISTRIBUTION AVAILIBILITY STATEMENT

Approved for Public Release; Distribution Unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The abstract is below since many authors do not follow the 200 word limit

14. SUBJECT TERMS

Chemistry; Liquid Crystals; Anchoring; Detection; Protection; Passive Sensors

15. NUMBER OF PAGES

Unknown due to possible attachments

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION ON THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev .2-89)
Prescribed by ANSI Std.
239-18 298-102

Report Title

New Tools for Measurement of Personal Exposure to Chemical Environments

ABSTRACT

The primary objective of this research was to demonstrate principles based on the orientational behavior of liquid crystals at chemically functionalized surfaces for passive sensing of targeted toxic gases, including chemical warfare agents. Included in this research was the systematic study of the competitive interactions of thermotropic liquid crystals and P-, N- and S-containing compounds with surfaces presenting metal carboxylates. Emphasis was directed to developing principles that lead to highly sensitive and selective ordering transitions in liquid crystals upon exposure of the liquid crystals to targeted chemical agents. ARO support enabled development of a fundamental understanding of metal ion-ligand coordination interactions between liquid crystals possessing nitrile groups and surfaces presenting divalent and trivalent carboxylate complexes. This development relied heavily on the use of infrared spectroscopy and led to the design of chemically tailored surfaces that trigger ordering transitions in liquid crystals upon exposure to parts-per-billion concentrations of dimethylmethylphosphonate and half mustard. Recent experiments performed at DSTL have also demonstrated that these principles can be extended to selectively report VX, GB, GD and GA.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Yang, Kun-lin; Cadwell, Katie; Abbott, Nicholas L.. Contact printing of metal ions onto carboxylate-terminated self-assembled monolayers. Advanced Materials (Weinheim, Germany) (2003), 15(21), 1819-1823.

Follonier, S.; Miller, W. J. W.; Abbott, N. L.; Knoesen, A. Characterization of the Molecular Orientation of Self-Assembled Monolayers of Alkanethiols on Obliquely Deposited Gold Films by Using Infrared-Visible Sum-Frequency Spectroscopy. Langmuir (2003), 19(25), 10501-10509.

Luk, Yan-Yeung; Abbott, Nicholas L.. Surface-Driven Switching of Liquid Crystals Using Redox- Active Groups on Electrodes. Science (Washington, DC, United States) (2003), 301(5633), 623-626.

Shah, R.R.; Abbott, N.L. "Orientational Transitions of Liquid Crystals Driven by Binding of Organoamines to Carboxylic Acids Presented at Surfaces with Nanometer-Scale Topography", Langmuir, (2003), 19(2), 275-284.

Yang KL, Cadwell K, Abbott NL
Mechanistic study of the anchoring behavior of liquid crystals supported on metal salts and their orientational responses to dimethyl methylphosphonate
JOURNAL OF PHYSICAL CHEMISTRY B 108 (52): 20180-20186, 2004

Yang KL, Cadwell K, Abbott NL
Use of self-assembled monolayers, metal ions and smectic liquid crystals to detect organophosphonates
SENSORS AND ACTUATORS B-CHEMICAL 104 (1): 50-56, 2005

Title: Deciphering the interactions between liquid crystals and chemically functionalized surfaces: Role of hydrogen bonding on orientations of liquid crystals
Author(s): Luk YY, Yang KL, Cadwell K, Abbott NL
Source: SURFACE SCIENCE 570 (1-2): 43-52, 2004

Lockwood NA, de Pablo JJ, Abbott NL
Influence of surfactant tail branching and organization on the orientation of liquid crystals at aqueous-liquid crystal interfaces
LANGMUIR 21 (15): 6805-6814, 2005

Guzman O, Abbott NL, de Pablo JJ
Quenched disorder in a liquid-crystal biosensor: Adsorbed nanoparticles at confining walls
JOURNAL OF CHEMICAL PHYSICS 122 (18) 2005

Grollau S, Guzman O, Abbott NL Slow dynamics of thin nematic films in the presence of adsorbed nanoparticles
JOURNAL OF CHEMICAL PHYSICS 122 (2) 2005

Clare, B. H.; Guzman, O.; de Pablo, J. J.; Abbott, N. L. "Measurement of the Azimuthal Anchoring Energy of Liquid Crystals in Contact with Oligo(ethylene glycol)-Terminated Self-Assembled Monolayers Supported on Obliquely Deposited Gold Films" Langmuir; 2006; 22(10); 4654-4659.

Liu XS, Jang CH, Zheng F, Jurgensen A, Denlinger JD, Dickson KA, Raines RT, Abbott NL, Himpsel FJ "Characterization of protein immobilization at silver surfaces by near edge X-ray absorption fine structure spectroscopy", Langmuir, 22 (18): 7719-7725, 2006

Katie D. Cadwell, Mahriah E. Alf and Nicholas L. Abbott, "Infrared Spectroscopy of Competitive Interactions Between Liquid Crystals, Metal Salts and Dimethyl Methylphosphonate at Surfaces" Journal of Physical Chemistry B, 2006, in press.

Joon-Seo Park, Chang-Hyun Jang, Matthew L. Tingey, Aaron M. Lowe, and Nicholas L. Abbott, "Influence of 4-Cyano-4'-Biphenylcarboxylic Acid on the Orientational Ordering of Cyanobiphenyl Liquid Crystals at Chemically Functionalized Surfaces", Journal of Colloid and Interface Science, 2006, in press.

Number of Papers published in peer-reviewed journals: 14.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

American Chemical Society Meeting, New Orleans, "Liquid Crystals on Nanostructured Surfaces and Nano-Scale Sensing", March, 2003.

American Chemical Society Meeting, New Orleans, "Adsorption of Amphiphiles at Interfaces Between Thermotropic Liquid Crystals and Aqueous Phases", March, 2003.

Chemical Engineering Seminar, University of Colorado, Boulder, "Amplification of Biomolecular Interactions using Liquid Crystals", March 2003.

Materials Research Society Meeting, San Francisco, "Biophotonics Based on Liquid Crystals and Nanostructured Surfaces", April 2003.

General Electric, Schenectady, "Liquid Crystals on Nanostructured Surfaces: Principles for Chemical and Biological Sensing", May, 2003.

Edgewood Chemical and Biological Command, Edgewood, "Principles for Chemical and Biological Detection using Surface-Driven Orientational Transitions of Liquid Crystals", August, 2003.

Geomotors Inc, Washington DC, "Amplification of Bio/molecular Interaction using Liquid Crystals, October 2003.

North Carolina State University, Department of Chemical Engineering, North Carolina, "Liquid Crystals as Amplifiers of Interfacial Phenomena", October 2003.

Center for Biologically Inspired Materials and Materials Systems, Duke University, "Liquid Crystals as Amplifiers of Biomolecular Interactions", November, 2003.

Plenary Lecture at the 2003 Annual Meeting of Japan Research Institute of Material Technology, Noday City, Japan, "Liquid Crystals as Amplifiers of Molecular and Biomolecular Interactions on Chemically Functionalized Interfaces", December, 2003.

Departmental Seminar, Chemical Engineering, Notre Dame University, Sept, 2004.

Seminar, Defense Science and Technology Laboratory, Porton Downs, UK, Sept 2004.

First Conference of Society of Bioengineering, Singapore, Sept 2004.

Army Research Office Workshop, Jackson Hole, WY, October, 2004

Departmental Seminar, Chemical Engineering and Materials Science, University of Minnesota, November 2004.

Departmental Seminar, Chemical Engineering, University of Iowa, December 2004.

Joint AIChE-IIT Meeting in Mumbai, India, December 2004.

Departmental Seminar, Yale University, February, 2005.

Seminar, Cargill, St Paul, March, 2005.

ACS Meeting, San Diego, March, 2005.

Materials Research Society Meeting, San Francisco, March 2005.

Gordon Research Conference on Liquid Crystals, New Hampshire, June 2005.

Pacifichem, Honolulu, December, 2005.

International Liquid Crystal Conference, Keystone, Colorado, July 2006.

Number of Presentations: 24.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

(d) Manuscripts

Number of Manuscripts: 0.00

Number of Inventions:

Graduate Students

NAME	PERCENT_SUPPORTED	
Katie Cadwell	0.63	No
Brian Clare	0.25	No
FTE Equivalent:	**0.88**	
Total Number:	**2**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED	
Kun-Lin Yang	1.00	No
FTE Equivalent:	**1.00**	
Total Number:	**1**	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Nicholas Abbott	0.05	No
FTE Equivalent:	**0.05**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME	
Brian Clare	No
Total Number:	**1**

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Problem Studied:

This research was directed to the study of micrometer-thick films of thermotropic liquid crystals that were supported on nanostructured surfaces decorated with metal ion receptors that bind both liquid crystals and sulfur and phosphorus-containing compounds. This research sought to understand and design competitive molecular interactions between metal ion receptors, liquid crystals and targeted analytes that lead to easily visualized and quantified changes in the orientations of films of liquid crystals upon exposure to sulfur and phosphorous-containing compounds. The primary objective of this research was to demonstrate principles based on the orientational behavior of liquid crystals at chemically functionalized surfaces for passive sensing of targeted toxic gases, including chemical warfare agents. Included in this goal was the systematic study of the competitive interactions of thermotropic liquid crystals and P-, N- and S-containing compounds with surfaces presenting metal carboxylates. Emphasis was directed to developing principles that led to highly sensitive and selective ordering transitions in liquid crystals upon exposure of the liquid crystals to targeted chemical agents. ARO support has enabled development of a fundamental understanding of metal ion-ligand coordination interactions between liquid crystals possessing nitrile groups and surfaces presenting divalent and trivalent carboxylate complexes. This development relied heavily on the use of infrared spectroscopy (see below for details) and has led to the design of chemically tailored surfaces that trigger ordering transitions in liquid crystals upon exposure to parts-per-billion concentrations of dimethylmethylphosphonate and half mustard. Recent experiments performed at DSTL demonstrate that these principles can be extended to selectively report VX, GB, GD and GA

Main Accomplishments:

Below we summarize the main elements of our accomplishments.

1. Sensitivity and Selectivity of the Liquid Crystal "E7" for Detection of Organophosphonates We investigated the orientational response of the liquid crystal E7 to DMMP. E7 is a commercially available LC that exhibits a nematic phase from -20^{o}C to +60^{o}C. We tested the orientational response of E7 supported on surfaces presenting copper carboxylate to dimethylmethyl-phosphonate (DMMP) at various concentrations in the parts-per-billions range. We determined that the sensitivity of E7 is better than 1 ppb,

with an onset response time around 10 s. Furthermore, the orientational response of E7 can be obtained without precise temperature control at room temperature. We have also determined that E7 shows good selectivity. It does not respond to 1% of saturated ethanol, hexane or acetone, and it does not respond to variations in humidity (up to ~80%).

2. High Throughput Screening of Metal Ion Receptors for Target Compounds: Correlation of Orientations of Liquid Crystals to Electron Affinity of Metal Ions. To screen for additional metal-ion receptors suitable for the detection of organophosphorous and organosulfur compounds, we have developed a simple and relatively high throughput screening system based on confinement of nematic 5CB in TEM gold grids (pitch ~ 300 μm and depth ~ 20 μm). Before exposure to DMMP, only Cu^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, La^{3+}, Al^{3+}, Eu^{3+} and Fe^{3+} showed homeotropic anchoring. The optical appearance of the LC thin films supported on the salts correlated well with the electron affinities of metal ions. These results have led us to conclude that 5CB on metal salts exhibit homeotropic anchoring when the electron affinity of the metal ion exceeds 15.6 eV and exhibit planar (or tilt) anchoring when the electron affinity is below 15.6 eV/s. All LCs were then exposed to 100 ppb DMMP vapor for 1 h. In addition to Cu^{2+}, we have identified two more metal ions, Al^{3+} and Eu^{3+}, as good DMMP receptors.

3. Polarization-Modulation IR reflectance-absorbance spectroscopy (PM-IRRAS) Studies of Liquid Crystals at Surfaces Relevant to Chemical Sensing. To understand better the nature of the interaction between the liquid crystal and the metal salts decorated on the surfaces, we used PM-IRRAS to compare the nitrile stretch peaks (at 2230 cm^{-1}) of 8CB supported on metal ions complexed to carboxylate-terminated SAMs. In the presence of copper ions, a new peak emerged at 2280 cm^{-1}, providing spectroscopic evidence of formation of a Cu^{2+}- nitrile group complex. Similarly, 8CB supported on nickel and cadmium showed a new peak at 2274 cm^{-1} and 2260 cm^{-1}, respectively. In contrast, 8CB supported on sodium and carboxylate-terminated SAMs without metal ions showed no new nitrile stretching peak. These spectroscopic measurements correlate closely with our observations of the anchoring of 5CB on metal salts: On surfaces presenting Cu^{2+}, Ni^{2+}, and Cd^{2+}, 5CB exhibits homeotropic anchoring, while on surfaces presenting Na^{+} and carboxylic functional groups, 5CB exhibit planar (or tilted) anchoring.

4. Stability of Thin Films of Smectic Liquid Crystals, and their Orientational Response to DMMP. Unlike nematic LCs, smectic LCs form stable,

micrometer-thick films when deposited onto the surfaces of solids. Therefore, thin films of the smectic LC, 4'-octyl-4-biphenyl-carbonitrile (8CB) supported on surfaces presenting copper ions were prepared by spin-coating and their orientational response to DMMP was investigated. We concluded that the system permits detection of DMMP at concentrations of 20 ppbv with response times of 20 s. In contrast, LC exposed to nitrogen shows no response. Because the orientational transition is reversible, we infer that the formation of the DMMP-copper ion complex is also reversible. Our study also demonstrates that the system exhibits molecular specificity. The system does not respond to water (up to 75% relative humidity) or common volatile organic compounds (VOCs) such as ethanol, hexane and acetone (1% saturated vapor). A limitation of the use of smectic liquid crystals, however, appears to be their high sensitivity to variations in temperature. The orientational transition triggered by DMMP was observed only at temperatures close to the smectic-to-nematic transition point.

5. Frustrated Structures in Liquid Crystals: Diffractive Optics for Stand-Off Detection. In addition to forming more stable thin films when deposited onto solid substrates, smectic LCs have other advantages over nematic LCs such as they diffract light strongly and give hexagonal diffraction pattern when a frustrated structure is formed among mesogens. We have demonstrated that a frustrated structure is formed when 8CB is sandwiched between two self-assembled monolayers which give 8CB planar and homeotropic orientations, respectively. Moreover, we showed that the hexagonal diffraction pattern caused by the frustration structure of 8CB can be erased when a surface-driven orientational transition of 8CB is triggered by the binding of DMMP to the copper ions. The results of this study suggest an approach to stand-off detection of organic compounds using smectic LCs. Our results also showed hysteresis between the introduction and release of the frustration structure when surface-driven orientational transitions occur, which may offer an explanation for the temperature-sensitive orientational transition in 8CB film as described above.

*6. Detection of Half-Mustard using Liquid Crystals. T*he high throughput system described above was used to screen metal-ion receptors for the detection of half mustard gas (2-chloroethyl methyl sulfide). We have identified four metal ions, Cu^{2+}, Eu^{3+}, Al^{3+} and Fe^{3+} as good receptors for half mustard gas and the orientational response of LCs supported on these metal ions to 100 ppb half mustard were studied. The dynamic response of 5CB supported on metal ions has the following order: $Cu^{2+} > Eu^{3+} > Al^{3+} > Fe^{3+}$. We also studied the initial response of LC supported on Cu^{2+} to DMMP vapor from

10 ppb to 1 ppm. It was determined that the sensitivity of 5CB is approximately 3 ppb, and the time-dependent intensity of light transmission through 5CB films correlates well with the half-mustard concentrations.

7. Competitive Binding of Mesogens and DMMP to Metal Ions by Transmission FTIR. We have used transmission FTIR to study the competitive binding of mesogens and DMMP to metal ions. Metal ions of perchlorate salts dissolved in benzonitrile were chosen as our model system to mimic LCs supported on metal ions because benzonitrile has similar chemical functionality to 5CB and 8CB. The shift in the absorption corresponding to the nitrile stretch in benzonitrile solution containing metal ions increased with the increase of electron affinities of metal ions. After 10 mM of DMMP was added to the benzonitrile, the new peak corresponding to the metal complex of nitrile groups diminished. These FTIR results are consistent with our proposition that DMMP binds stronger to metal ions and displaced the weakly bounded nitrile groups from metal ions.

8. Characterization of Binding of DMMP to Surfaces Presenting Cu2+ Salts. We have performed some new experiments aimed at providing an experimental characterization of the competitive binding of DMMP to surfaces presenting Cu2+ salts complexed to 5CB. We have fabricated a flow cell that can be filled with known concentrations of DMMP and inserted into the optical path of our PM-IRRAS instrument. We have obtained compelling evidence that the nitrile group of the liquid crystal is perturbed in its coordination with Cu2+ upon introduction of DMMP into the system. This result provides experimental evidence in support of our proposed mechanism of competitive interactions at the Cu2+ surface. The have also obtained spectroscopic evidence of the formation of a coordination complex between the phosphoryl group of DMMP and the Cu2+ ions on the surface.

9. Influence of Chiral Dopants. We believe that frustration introduced into liquid crystals by the addition of chiral dopants can form the basis of passive sensors that possess sensitivities which are substantially higher than those that we have already demonstrated (ppb). Towards this goal, we have investigated the influence of chiral dopants on surface driven anchoring transitions. We have observed that surface driven anchoring transitions lead to easily observed changes in the characteristic “fingerprint” texture of a chiral nematic phase of liquid crystal. These changes in the fingerprint pattern may also provide avenues to measurements of the strength of interaction of the liquid crystal with the

surface. Measurements of strengths of interaction (anchoring energies) will provide a new avenue to quantification of the responses of LCs to target gas phase analytes.

10. Demonstration of the Application of Principles to Detection of VX, GB, GD and GA. In December 2005, we traveled to DSTL at Porton Downs, UK, and performed feasibility studies aimed at validation of our approaches using live agents. These experiments were successful, leading to the identification of metal ions and liquid crystals that permit detection of vapors of VX, GD, GB and GA.